Determination of Mechanical and Surface Properties of Semicrystalline Polyhedral Oligomeric Silsesquioxane (POSS) Nanocomposites

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Overview

- Introduction
- Experimental
- Results and Discussion
- Conclusions
- Acknowledgements

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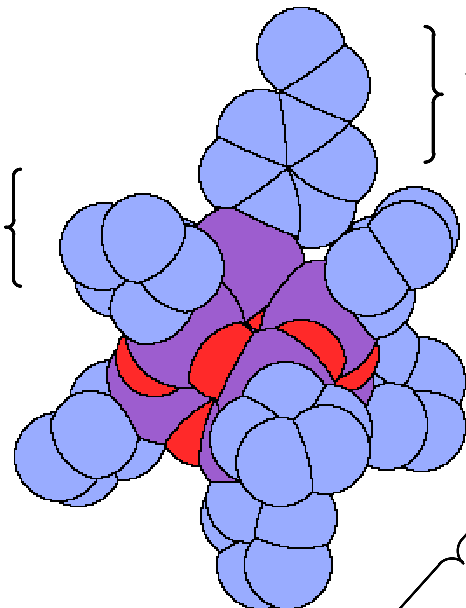
Introduction

- **Nanomodification of semicrystalline polymers**
  - **unequalled thermal, mechanical and surface properties at low volume fractions that cannot be obtained using conventional fillers**
- **Blending POSS molecules into polymers can increase the thermal and mechanical properties as well as the surface properties**
- **The objective of this study is to examine the effect of blending various POSS molecules into a variety of appropriate semicrystalline polymers.**

Anatomy of a POSS Nanostructure

Nonreactive organic (R) groups for solubilization and compatibilization.

Nanoscopic in size with an Si-Si distance of 0.5 nm and a R-R distance of 1.5 nm.



May posess one or more functional groups suitable for polymerization or grafting.

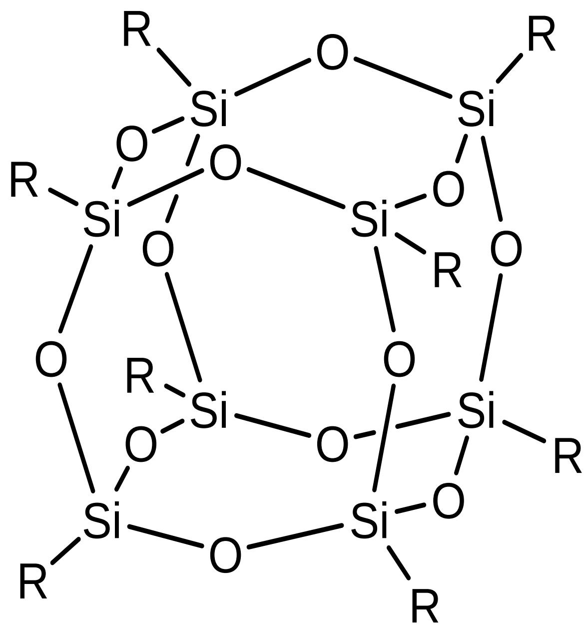
Thermally and chemically robust hybrid (organic-inorganic) framework.

Precise three-dimensional structure for molecular level reinforcement of polymer segments and coils.

Background

- **Bruce Fu and coworkers**
  - **Methyl$_8$T$_8$ into ethylene-propylene copolymers yielded 70% increase in the Young's Modulus.**
  - **POSS molecules crystallized and these nanocrystals formed weak bonds with the polymer chains.**
- **Unpublished results indicate that this reinforcement is not seen in polyethylene homopolymer blends.**
  - **Methyl pendant group on the polymer chain is influencing the reinforcing efficiency of the POSS molecules**
- **The primary reinforcing mechanism in the nanocomposites, POSS/POSS interactions, POSS/polymer interactions or a combination of the two, is a subject for future research.**

Materials



Fluorooctyl$_8$T$_8$

R = $-CH_2CH_2(CF_2)_5CF_3$

Fluorodecyl$_8$T$_8$

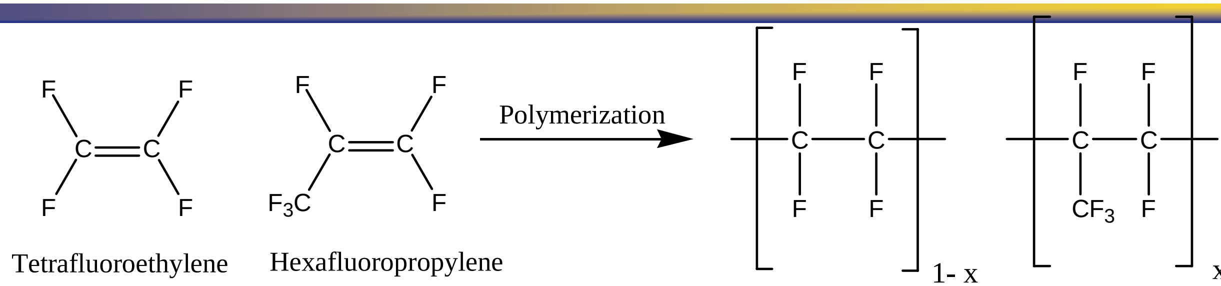
R = $-CH_2CH_2(CF_2)_7CF_3$

Methyl$_8$T$_8$

R = Methyl

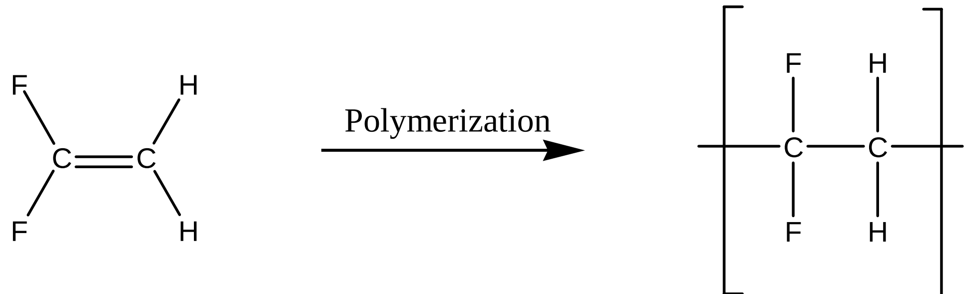
POSS (polyhedral oligomeric silsesquioxane)

Blend Preparation



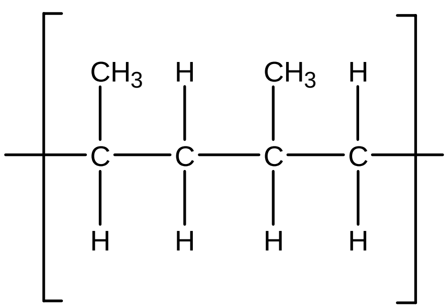
Tetrafluoroethylene Hexafluoropropylene

FEP



Vinylidene fluoride

PVdF

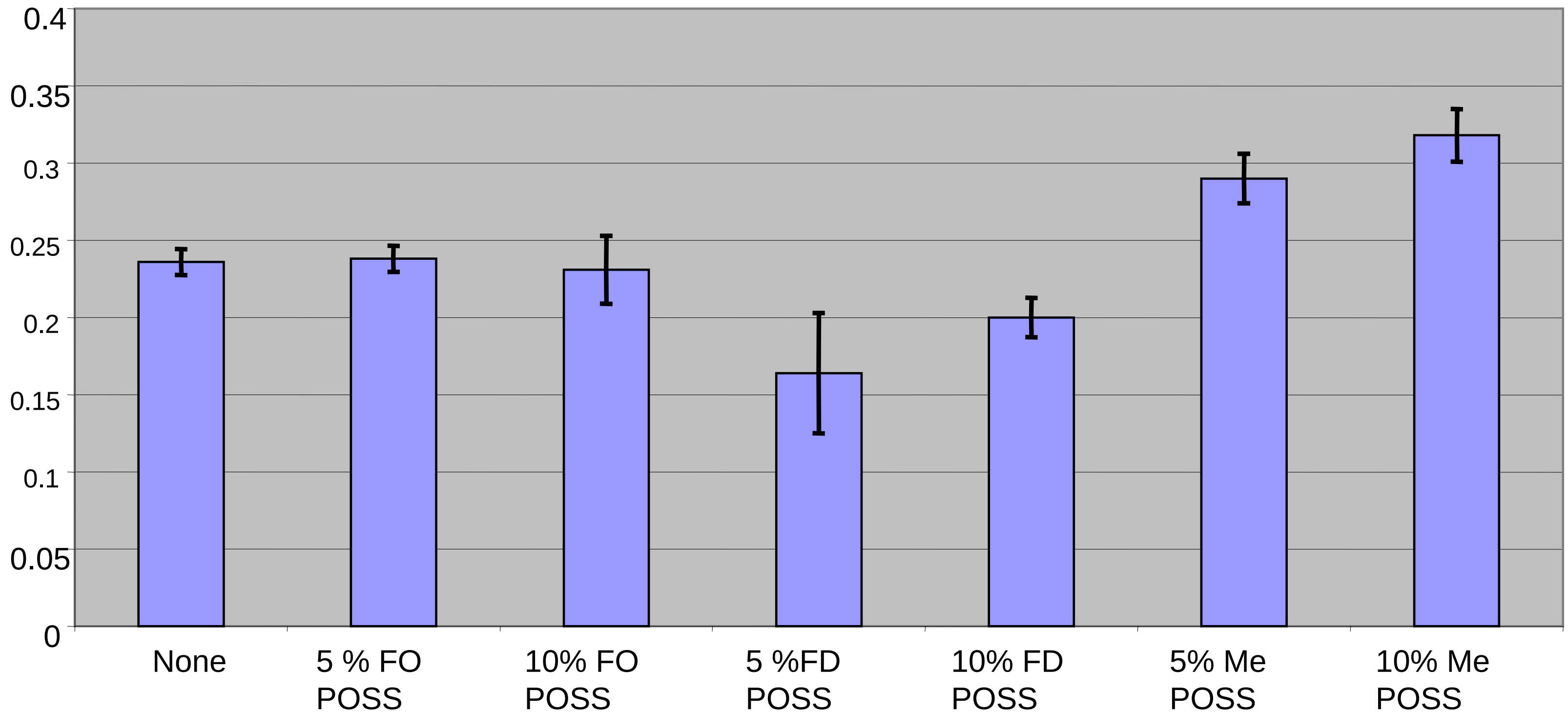


Isotactic polypropylene

Blend Preparation

- Five and ten weight percent of methyl$_8$T$_8$, Fluorooctyl$_8$T$_8$ and fluorodecyl$_8$T$_8$ melt blended into FEP and PVDF using a DSM Microcompounder
  - Mixed under nitrogen at screw speed of 100 RPM
  - FEP blends compounded at 280 ºC for three minutes
  - PVDF blends mixed at 180°C for three minutes
  - Injection molded directly from microcompounder
- Five and ten weight percent methyl$_8$T$_8$ blended into PP using a DSM Minicompounder.
  - PP blends processed at 220 ºC for ten minutes

Results and Discussion



- **$Methyl_8T_8$ blended into FEP**
  - **25% increase in modulus**
  - **No difference between 5 and 10 wt% of filler**
- **$Fluorodecyl_8T_8$ or $fluorooctyl_8T_8$**
  - **No difference in modulus from unfilled FEP**
  - **Inconsistent results**

Results and Discussion

- **Blends with FEP and either fluorodecyl$_8$T$_8$ or fluorooctyl$_8$T$_8$**
  - **Lower yield points, between 7-8 MPa, when compared to unfilled FEP, 10.5-12.5 MPa range.**
- **Blends with FEP and methyl$_8$T$_8$**
  - **No significant change in yield point compared to unfilled FEP**

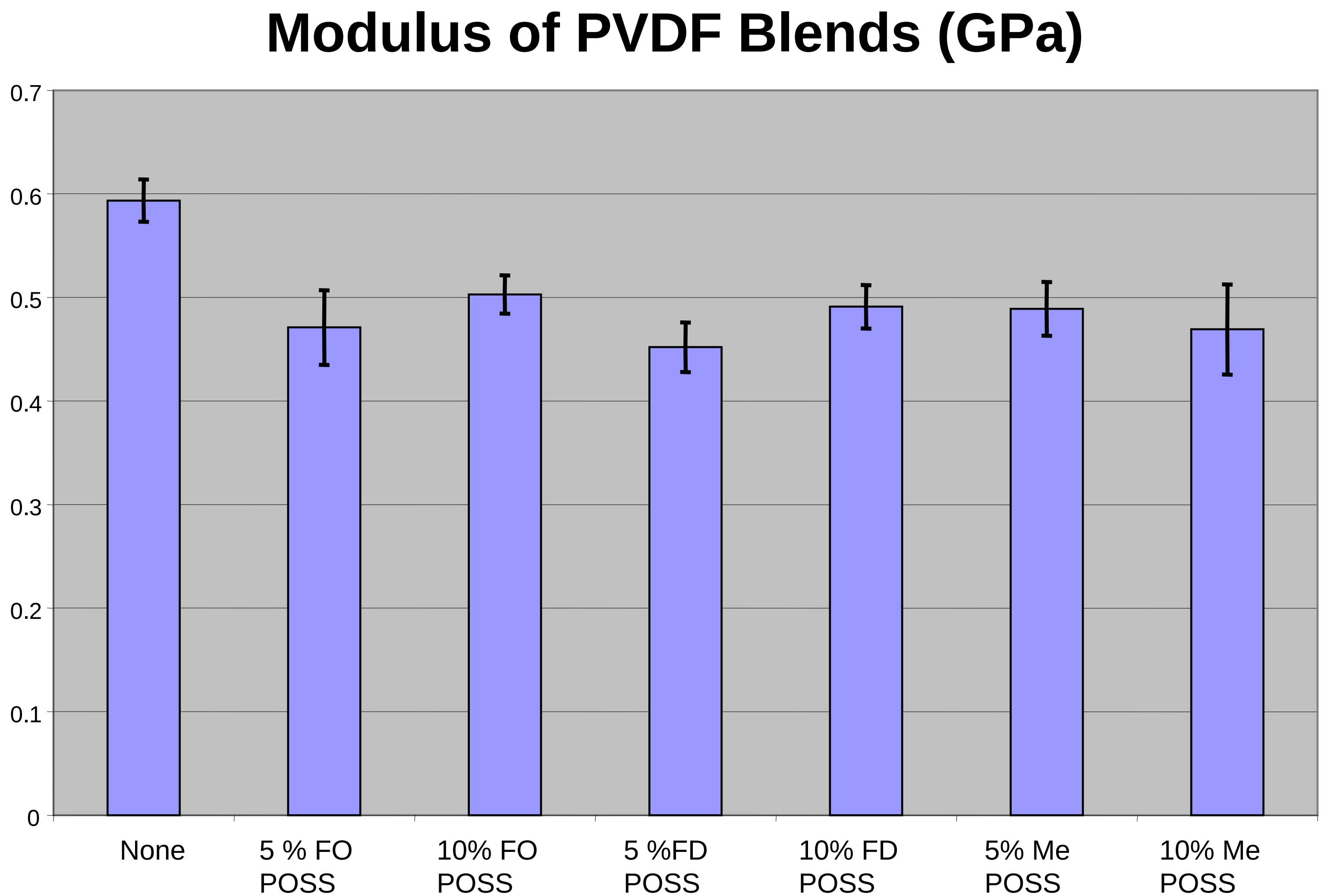
Results and Discussion

- **Data gathered for FEP filled with fluorodecyl$_8$T$_8$ or fluorooctyl$_8$T$_8$ inconsistent**
  - **Outer layers of tensile bar flaked away as soon as tension was applied**
  - **Interior of the tensile bars frequently elongated to over 150% strain before breaking**
  - **Indirect evidence of surface migration of the nanoparticles with a core/shell morphology**
  - **Each region has different physical properties**

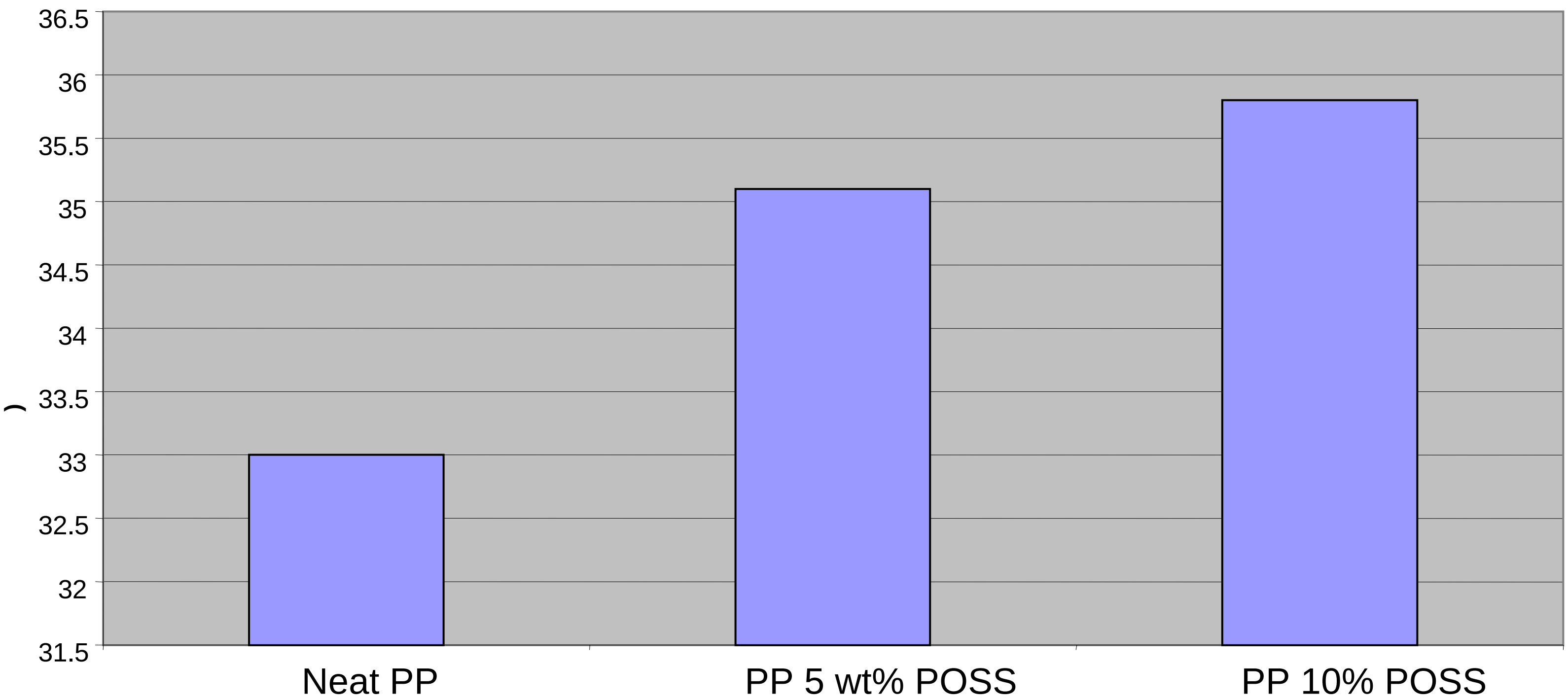
Results and Discussion

- **PVDF samples**
  - **Elongated until failure**
    - **55% PVDF**
    - **Average of 80% nanofilled PVDF**
  - **All fillers lowered the modulus**
    - **On average 20% decrease**
  - **This may imply that there is a uniform concentration of the POSS throughout the sample**
  - **No significant difference was found among the various types of fillers or different loadings**
- **Unfilled PVDF samples had a slightly higher yield point (40.0 MPa) than did any of the POSS filled samples (36.0-37.5 MPa range)**

Results and Discussion

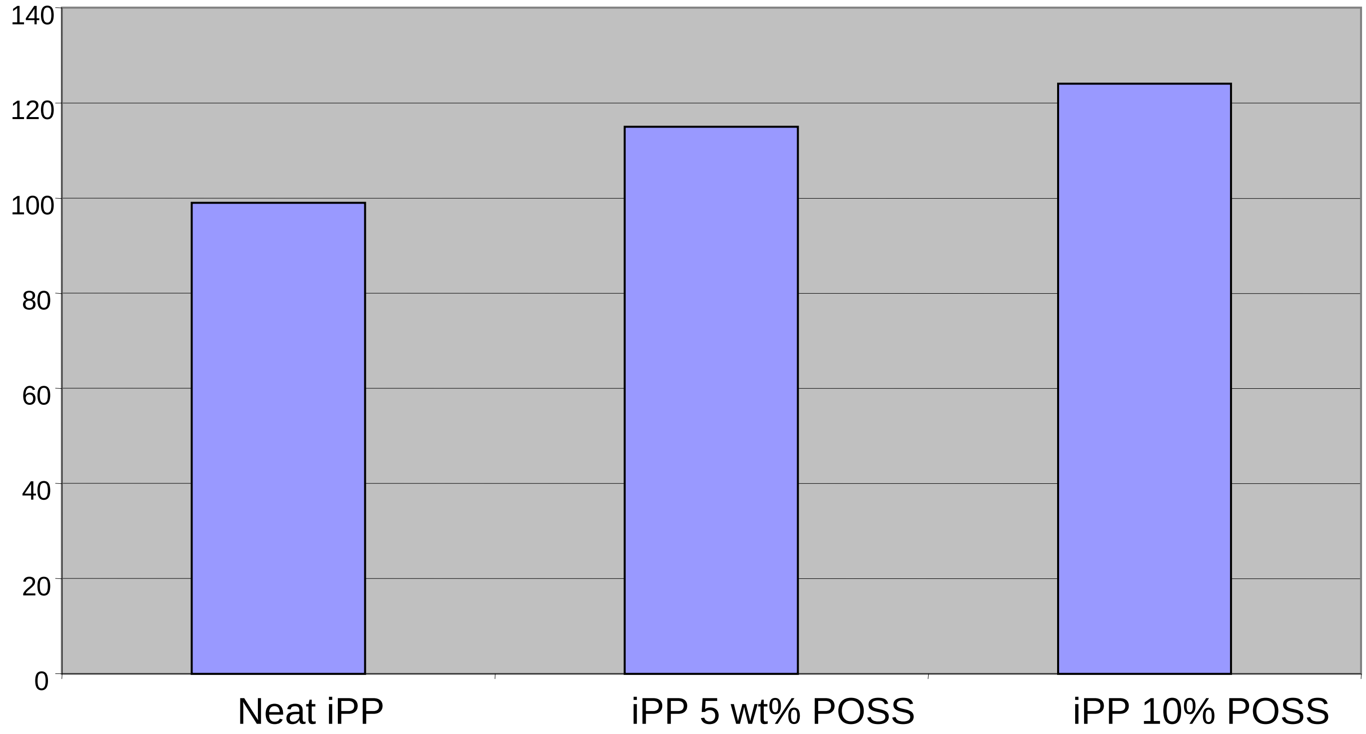


Tensile Strength of PP Blends (MPa)



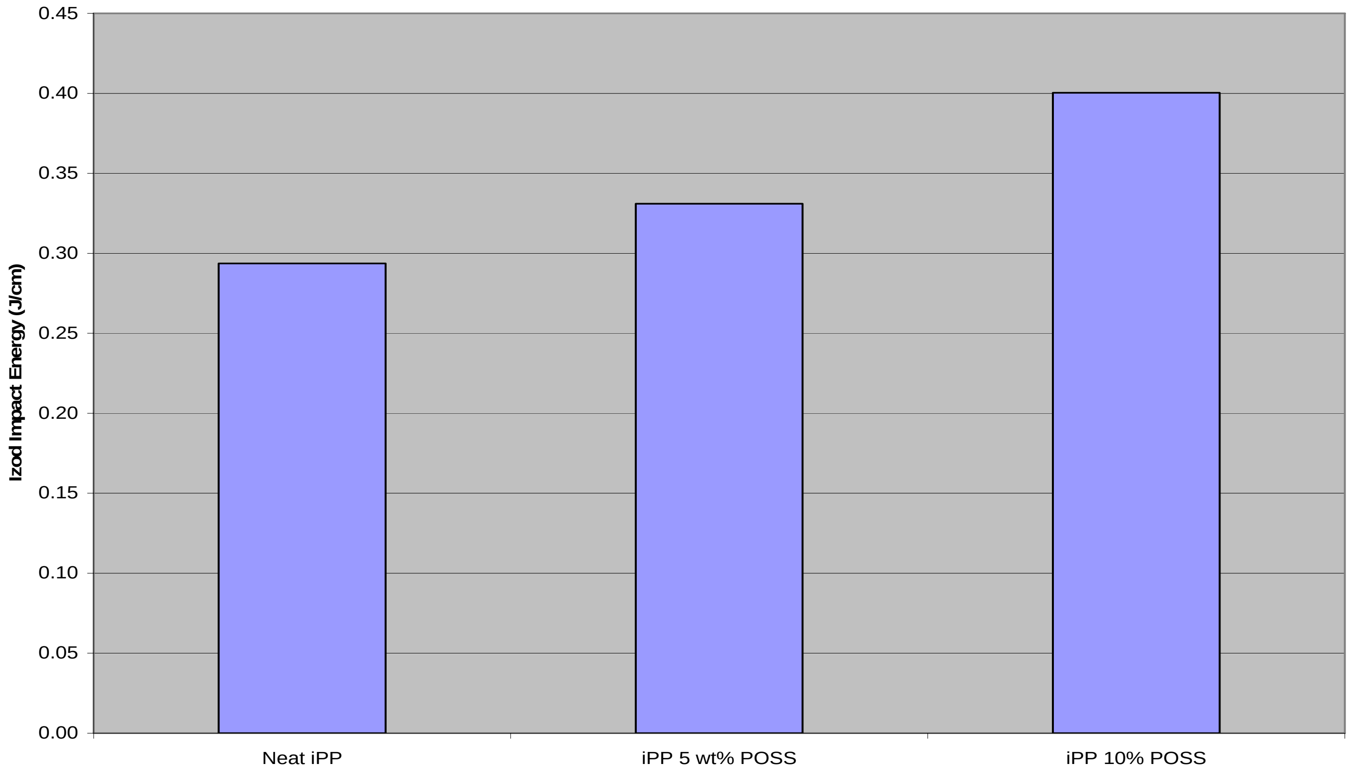
- **Methyl$_8$T$_8$/PP blends showed a minor increase (5-10%) in tensile strength compared to neat blends**
- **Contrasting results due to the different compatibilities of the methyl$_8$T$_8$ with FEP and PP**
- **Methyl$_8$T$_8$ has a higher affinity for the PP and thus has a stronger reinforcing capability**

Heat Distortion Temperature (°C)



- **Addition of POSS to PP yielded a substantial increase (15 – 25%) in heat distortion temperature**
- **Increase is due to interactions between the POSS crystallites and polymer crystallites**

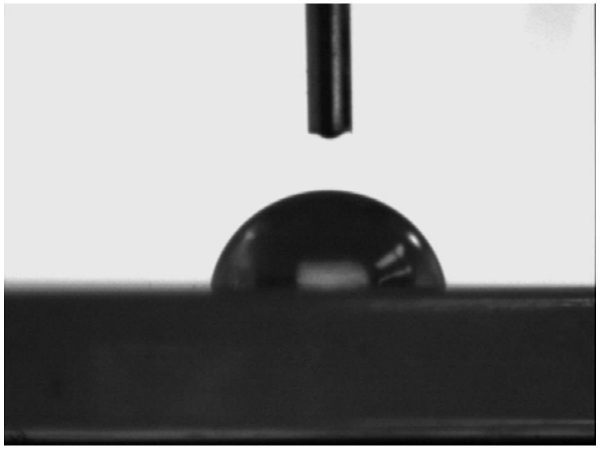
Impact Strength



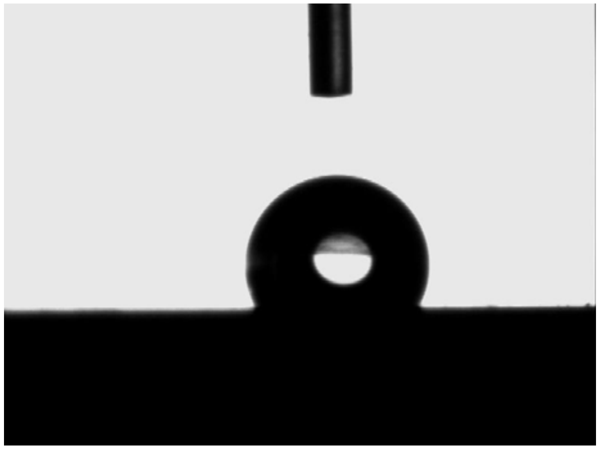
- **The addition of modulus increasing nanoparticles actually increases the impact properties (15 – 40% increase)**
- **Increase may be derived from the nanodispersion of the POSS crystallites, which are not large enough to create stress concentrations, and the reinforcing ability of the POSS crystallites.**

Results and Discussion

- Addition of fluorodecyl$_8$T$_8$ and fluorooctyl$_8$T$_8$ greatly increased the hydrophobicity of PVDF blends
  - 5 wt % of either material increased contact angle from ~70° for unfilled PVDF to between 105-110°
- Addition of 10 wt % of FluoroPOSS yielded angles as high as 116°
- Addition of methyl$_8$T$_8$ to PVDF showed a more modest increase in hydrophobicity, but still an improvement over the unfilled material



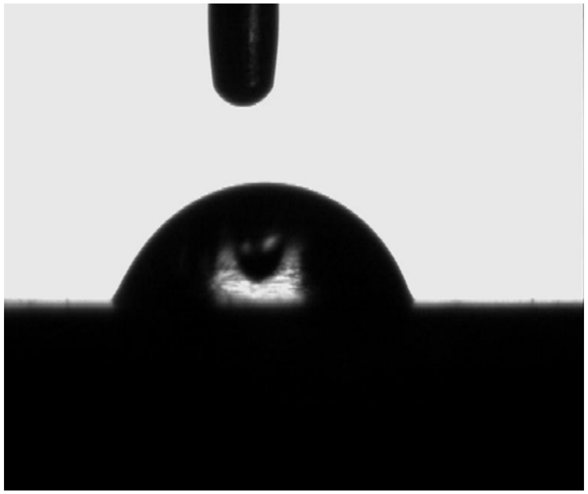
PVDF



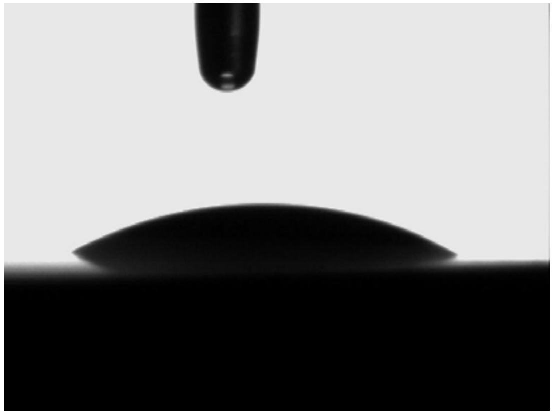
PVDF w/10 wt% fluorooctyl8T8

Results and Discussion

- **Fluorodecyl$_8$T$_8$ and fluorooctyl$_8$T$_8$ increased the oleophobicity of PVDF**
  - **Unfilled PVDF samples yielded contact angles around 25°**
  - **Addition of fluorodecyl$_8$T$_8$ yielded contact angles greater than 70°**
  - **Addition of fluorooctyl$_8$T$_8$ yielded contact angles greater than 50°**
- **Addition of methyl$_8$T$_8$ decreased the oleophobicity of PVDF**



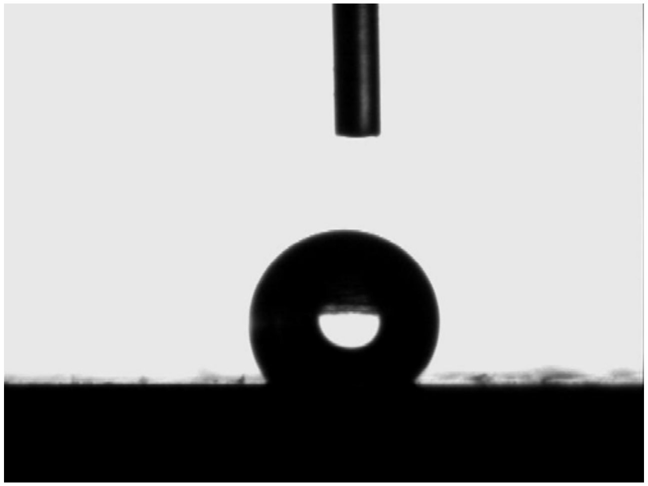
PVDF 5wt% Fluorooctyl8T8



PVDF

Results and Discussion

- **FEP filled with methyl$_8$T$_8$ yielded contact angles as high as 126°**



FEP 10% methyl8T8

- **Surface of injection molded FEP samples was uneven**
  - **Contact angle measurements were inconsistent**
  - **Top layer polished off with very fine sandpaper**
  - **After polishing, contact angles were in the same range as those found for unfilled FEP samples**
  - **Either flow patterns during injection molding or surface migration may be pushing the fillers toward the surface**

Conclusions

- **FluoroPOSS blended into PVDF lowered the modulus**
  - **No significant difference was observed among different fillers**
  - **Slightly lower yield points were observed for the filled versus unfilled PVDF blends**
- **FEP blends showed indirect evidence of surface migration, as evident in core/shell morphology of injection molded tensile bars**
  - **Nanoparticles may not be evenly distributed**
  - **$Methyl_8T_8$ significantly increased the modulus of FEP blends**

Conclusions

- POSS added to polypropylene/methyl$_8$T$_8$
  - Increased heat distortion temperature by about 25%
  - Increased impact energy by over 35%
  - Tensile strength increased with the addition of POSS
- Water and organic contact angles
  - FluoroPOSS blended into fluoropolymers increased the water and organic contact angles
  - Addition of methyl$_8$T$_8$ to PVDF decreased the oleophobicity, but increased the hydrophobicity

Summary and Conclusions

- FEP w/POSS
- Core/Shell Morphology
  - Surface Migration – Functionally graded materials
  - Non-uniform dispersion – Poor processing
- Mechanical Properties
  - FluoroPOSS – no difference in modulus, lower yield stress
  - $Methyl_8T_8$ – increase in modulus, neutral yield stresses
    - CH_3 group on $methyl_8T_8$ interacting with CF_3 group on FEP

Summary and Conclusions

- PVDF w/POSS
- Mechanical Properties
  - POSS decreased modulus
  - POSS decreased yield stress
  - No POSS/polymer chain interactions
- Contact angles
  - Water contact angles increased
  - Organic contact angles
    - Increased with incorporation of FluoroPOSS
    - Decreased with incorporation of methyl POSS

Summary and Conclusions

- **PP w/POSS**
- **Mechanical Properties**
  - **POSS increased Heat Distortion Temperature**
  - **POSS increased tensile strength**
  - **POSS increased IZOD impact strength**
- **Possible POSS/Polymer chain interactions**